PLASTICITY OF THE DAKOTA CLAYS OF KANSAS

by

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Approved,

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TABLE OF CONTENTS

PLASTICITY OF THE DAKOTA CLAYS OF KANSAS.

INTRODUCTION.

Plasticity of clays has been explained by many writers but few of them have reached similar conclusions. The early writers, Seger, in Europe, and Johnson and Blake in this country, endeavored to explain plasticity from the physical point of view. Later investigators began to study plasticity from the chemical point of view.

With the better understanding of physical chemistry and with a better knowledge of colloidal matter, inroads into the cause of plasticity from the physico-chemical direction were made by more recent investigators, for example, Ashley, in this country, has experimented with clays in order to explain the cause of plasticity by measuring the colloids of the clay. He was then able to obtain a relative measure between colloidal content of a clay and its plasticity.

Many investigators, working along this line, have come to the conclusion that the colloids of clay may consist of organic or inorganic matter. The inorganic colloids, they say, consist of aluminum or magnesium hydroxide, iron hydroxide, and colloidal silica. The organic colloids have not been definitely established. Some investigators, for example, John Stewart, believe that the organic colloids consist of organic salts of iron and alumina. Others have suggested that the organic colloids consist chiefly of humus matter. No definite conclusions can be found in literature

on this phase of the subject.

The aim of this paper is to first review the theories of plasticity, and second, by measuring their relative plasticity, to definitely point out the fact that clays of a same formation, or even at various depths of a single bed, varies in its plasticity.

To carry out this fact, about thirty clays of the Dakota formation from various parts of the State of Kansas were experimented with. Three sets of experiments were made, and the results and comparisons are tatulated in Chapter II.

The first experiment consisted in following the method established by Ashley, with a few minor changes, with malachite green. This establishes the relative plasticity of a clay by gauging the relative colloids in the clay. Against these results, shrinkage results are compared, and finally, the clays were subjected to the "feel" test. It is proven conclusively that the clays from one formation at varoius localities and depths vary greatly.

The writer wishes to express his especial indebtedness to Mr. Paul Teetor, Ceramic Engineer, Kansas University, who helped to arrange the outline of this investigation and also aided in shaping this report.

CHAPTER I

PLASTICITY IN GENERAL

Definition of Plasticity.

Plasticity, as defined by Seger (1), is that property of clay which engbles a solid to receive a liquid in its pores, to retain the latter completely, thus enabling the mass, by pressure and kneading, to retain the shape unchanged on the removal of pressure and extraction of the liquid and a consequent change to the solid state.

Ashley (2) defines plasticity as the combination of granular materials and colloids in such proportion that, when reduced to sufficiently fine size and properly moistened with an appropiate amount of water, plasticity is developed. If the colloidal matter is in exeess the clay is considered very plastic, fat, or sticky, but if the granular material is in excess, it is called sandy, weak, or non-plastic.

THEORIES OF PLASTICITY.

The various theories that have been advanced from time to time to explain the property of plasticity of clays has been well classified by N.B. Davis (3), and with a few additions and changes will be used as follows:

A - Structure of clay particles.

1 Fineness of grain

2 Plate structure

3 Interlocking particles

4 Sponge structure of the particles

B - Presence of Hydrous Aluminum silicates

C - Molecular attraction between particles

D - Inorganic colloidal matter

1 - Absorption theory

2 - Colloidal silica

3 - Iron and Aluminum Hydroxides.

E - Organic colloidal matter

1 - Organic matter in general

2 - Organic compounds of iron and aluminum

F - Humus compounds.

A - STRUCTURE OF CLAY PARTICLES

In 1867 Johnson and Blake, (4) working on Kaolinite, tried to explain plasticity as due to the fineness of grain, and plate structure of the Kaolinite and other platy materials present in the clay.

Clays in which they found bundles of Kaolinite crystals, seemed to be of lower plastic than those in which the bundles were broken up into their component plates.

R. T. Stull (5) ground mica and found a surprising increase in plasticity.

Atterburg concludes that the plasticity of European clays is due to the presence of mica meal in those of the north and to Kaolinite scales in those of the south.

Two Russian investigators (6) came to the conclusion that plasticity is due to the interlocking of the clay parti-

cles and depends for its best development upon a proper mixture of very fine and coarse particles.

Daubré (7) found that long continued grinding of feldspar developed some plasticity, and Olchewsky (8) explained this as due to the porous spongy structure of the finest particles caused by removal of the alkalies in solution.

B - PRESENCE OF HYDROUS ALUMINUM SILICATES.

Many investigators have brought forward the idea that the presence of hydrated silicates of aluminum as the cause of plasticity. It was noted that in general the temperature at which Kaolinite lost its water of constitution was coincident with the disappearance of plasticity, an assumption now known to be incorrect.

C - MOLECULAR ATTRACTION BETWEEN PARTICLES.

Grout was the first to develop this theory in any extent in connection with clays. He describes that plasticity is due to the following factors:

1 - The distance the clay particles can move on each other without losing coherence which varies with (a) shape and size of grain, (b) distance through the water film the particles will attract each other.

2 - The amount of coherence or resistance to movement, which varies with (a) the friction in the film, (b) the friction of the grains on each other.

COLLOIDAL MATTER

Before discussing those theories that attempt to explain plasticity as due to colloidal matter in the clay it would perhaps be best to lead up to it through a discussion of the present day conception of the colloidal state of matter.

Thomas Graham (9) an English physicist, working on his classical experiments 1860 - 64, on diffusion or dialysis was led to divide substances into two groups, according as the rate of diffusion is comparatively large or exceedingly small. Substances belonging to the latter group, he termed colloids, in contradiction to the rapidly diffusing group of crystalliods, which as its name implies, comprised for Graham substances which crystallizes well from (and are therefore fairly soluble in) water; the chief examples of this class are salts generally and soluble organic substances (e. g. sugar) of comparatively simple structure. The colloids on the other hand, were in general substances of very slight solubility in water, and in many cases of complex structure; the typical examples of this class are gelatin, gums, starch, etc.

Further work along this line showed that substances, formerly considered soluble, could be obtained in what appeared to be true solutions, yet they would not diffuse; these apparent solutions, he called colloidal, or "sols". Graham also found that slight additions of electrolytes, either acids or bases, which did not react chemically with the substances in colloidal solution, tended to precipitate it or

coagulate it. The coagulated sols he called "gels" because of their jell-like nature.

Since Graham's time many changes have been made in the socalled chemical theory of colloids. Recent investigations have shown that crystalliods may under certain conditions behave as colloids and conversely. For instance NaCl has been obtained in the colloidal form by Von Veimarn, (10) while on the other hand, it has been found by Paterno (11) that tannin and gallic acid, which in aqueous solutions are typical colloids, give, when dissolved in glacial acetic acid, freezing point depressions which corresponds to normal molecular weights, consequently solutions of these substances in acetic acid are to be regarded "true solutions".

Moreover, we are now in possession of ample evidence, obtained largely by means of the ultra-microscope, that there is a continuous progression as we pass from coarse visible suspensions through colloidal solutions to "true solutions" (12) and one substance may appear under proper conditions in any of these forms. Therefore, it is now generally concluded that it is not advisable to distinguish between colloid and crystalloid substances; that the term "colloid" is not descriptive of an inherent property of a substance, but of its properties in relation to one another. In other words, "the theories of colloidal chemistry do not deal with colloidal substances, but with the colloidal state of substances". Similarly, "colloidal phenomena are not, strictly speaking, the properties of colloidal substances, but are the peculiarities

which are exhibited as a first approximation by a given substance, when it is observed in the colloidal state." *

This change in view point has resulted in a change of nomenclature, so that it is now usual to speak of the "disperse phase" and the "dispersive medium", the former for the "colloid", and the latter to designate the constituent of the "colloidal solution"; the new terms are preferable because they imply nothing except the obvious fact that the colloidal state is not strictly homogeneous state of matter; in other words, in the colloidal state more than one phase** is present.

* The term "colloidal matter of clay" implies that water is the dispersive medium.

** A phase, in the physicochemical usage, is defined as a mass chemically and physically homegeneous or a mass of uniform concentration.

CLASSIFICATION OF DISPERSE SYSTEMS.

Many schemes of classification have been proposed, all more or less arbitrary. The most general scheme is that given by W.O. Ostwald (13) as follows: (This classification was also made independently by E. E. Free, in America.)(14)

Dispersive medium	DISPERSE PHASE Gaseous	Liquid	Solid
Gaseous	Class 9. G+G No real example as gases are always completely miscible.	Class 8. G+L. Fog e.g. other points of liquification of gases, atmospheric fog, etc.	Class 7 Smoke, cooled ammonium chloride vapor, etc.
Liquid	Class 6. L+G foams	Class 5 L+L Emulsions	Class 4 S+S. Suspensions, gels.
Solid	Class 3. S+G Gas Inclusions in minerals (pumice) or in metals	Class 2. S+L Liquid inclusions in minerals; occluded water, water of crystallization	Class 1. S+S Inclusions of solid particles in minerals; solid solutions.
G = Gas.	L = liquid	S = solid	

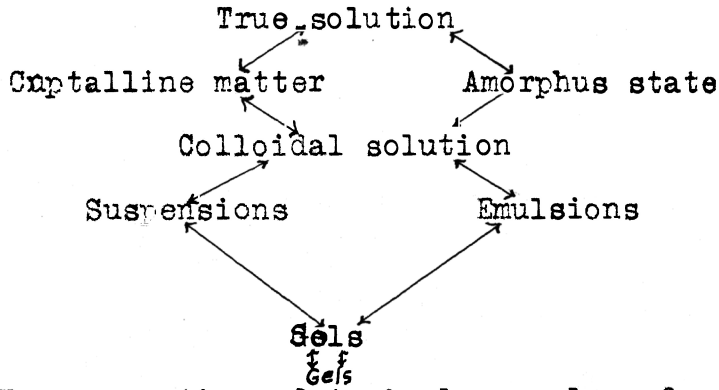
It is, of course, obvious that no hard and fast distinction can be drawn, for there is a continuous change of

properties as we pass from one class to another. The above classification is given merely to show the generality of the phenomenon of dispersion and because such a scheme may aid in applying the results and conclusions with one class to another.

Emulsions and suspensiods colloids (Emulsiods and Suspensoids)

These two groups make up what has been termed "colloidal Chemistry", and are by far the most important of all the groups.

The two groups fall under the liquid-solid and the liquid-liquid systems. Any substance, amorphous or crystalline may take on the colloidal condition, and there is a tendency toward an equilibrium between these three states and true solution. This may be represented diagramatically as follows;



The properties of typical examples of each group show marked divergencies, and accordingly they have been distinguished by various names. Thus, H. A. Noyes calls them "Colloidal solution"and " colloidal suspension", respectively; the former characterized as "viscous, gelatinizing"colloidal

mixtures, not easily coagulated by salts," and the latter as non-viscous, non-gelatinizing, but readily coagulable mixtures." These have been termed "lyophile" and "lyophobe". Practically the same distinctions are made in the terms "sol" and "gel", which, however, are often more loosely used. Generally, the word "sol" is used to denote colloidal conditions similar to typical gold sols or sols of other metals; gels to denote galatinous or jelly-like colloids. No definite distinction can be made between these two; thus the collodial alumina and ailica-constituents of the colliodal matter of clay and shale may appear in either form or change from one form to the other, according to conditions. Moreover, there is no sharp line of demarcation between emulsiods and "true solutions", on the one hand, and between suspensoids and coarse visible suspensions, on the other. This is equivalent to the statement that the properties of such disperse systems vary continuously with the degree of fineness of the particles of the disperse phase, or with the aggregate extent of its surface per unit of area; in other words, the properties may vary with the degree of dispersion. This has been best shown by P. P. VonViemarnon (15) the form in which $BaSO_4$ appears when it is precipitated by mixing equivalent solutions of barium thiocyanate and maganese sulphate in progressively increasing concentrations. These experiments showed that from the most dilute solutions crystal of measurable size formed with which increasing concentration diminished pro-

gressively from microscopic to ultra-microscopic; while from concentrated solutions colloid sols and finally gels of gradual increasing permanence were obtained.

Viscosity is another important property of fundamental importance in investigating the properties of the colloidal state, on account of the extreme sensitiveness of this constant toward very slight alterations in the condition of colloids. The metal and sulphide sols have been found to have very little effect on the viscosity of the solvent while organic sols have been found th show marked increase in viscosity. The organic sols are usually liquid (emulsions) and this has led us to consider that in colloidal solutions showing an increased viscosity, the disperse phase is a liquid.

It has been shown by Stokes (15) in 1850 that a small round particle falling in a liquid assumes a constant velocity; and as the radius of the particle becomes smaller, the rate of falling decreases. This explained by his formula as follows;

$$v \quad \frac{2r\,g}{9k}(d-d') \qquad \text{Where} \begin{cases} r \text{ is radius of spherical particle} \\ k \text{ is viscosity of fluid} \\ d \text{ and } d' \text{ density of fluid and particle respectively} \\ g \text{ acceleration of gravity} \\ v \text{ velocity of fall} \end{cases}$$

Hence, with very small particles, we may have a suspension that will appear stable for a long time. If the praticles

are irregular in shape, as they usually are, the velocity of the fall is lower, due to increased resistance.

Besides gravity, other factors are to be considered in examining the stability of colloids. The most important, perhaps, is the electric charge taken by the particles when suspended in the liquid medium. Clay particles suspended in water take on a negative charge, and hence continually repel each other. This repulsion may be one cause of another phenomena known as the Brownian movements, so names after their discoverer Dr. Brown, and English Botanist The movement may be noticed in all colloidal suspensions. The particles are seen to be jumping around in all directions in the medium, yet not touching one another. This movement tends to keep the particles in suspension. Brownian movements are found, moreover, in all suspensions containing particles less than 0.004m.m (4μ) in diameter. It is shown strongly by clay suspensions. Indeed, Atterburg (16) defines clay as particles under 0.002m.m diameter, which shows Brownian movements strongly. (0.003 M.m show it only weakly).

W. H. Brown (17) noted that "those substances that retarded the " Brownian movements' hasten the prepricipitation of fine grained sand, flocculant clays, and pulverized charcoal when suspended in water.

The conclusion to be drawn from the foregoing discussion may be summed up as follows: To say that a substance is in colloidal state (with reference to another substance, water in practically every case) is equivalent to the state-

ment that the substance is dispersed through the water to form particles of which the diameter may range all the way from molecular up to microscopic and macroscopic dimensions. The size of the particles is determined by the method of formation of the disperse system (as it is now generally termed) . The properties exhibited by the system vary with the fineness of the particles (the degree of dispersion); consequently the phenomema produced in disperse systems by variations of the external conditions or by the addition of reagents- apart from purely chemical effects, such as the ordinary solvent effect of HCL upon colloidal ferric hydroxide- are due to variations in the degree of dispersion produced by the change of circumstances.

Phenomena of Flocculation and Deflocculation.

The process of coarsening or sedimentation of particles is now commonly termed flocculation. The opposite process, of deflocculation. In other words, suspensions are said to be deflocculation when they settle slowly or not at all. Both flocculation or deflocculation are relative only, for we have no means of measuring their extent. It is, however, convenient to speak of the degree of flocculation. Thus, when we say the addition of alkalies decreases the degree of flocculation, we understand that the alkali tends to deflocculate the system; or in other words, to decrease the size of disperse particles and so render the disperse system more permanent. Bothexternal circumstances

and the addition of foreign substances greatly effect the degree of flocculation. Again, the addition of stronger alkalies and organic colloids decrease the degree of flocculation while neutral salts and acids increase it. The former are termed "deflocculators" and the latter "flocculators.(18)

Hardy (19) states that a suspension (or colloid) will be flocculated by a solution or another suspension whose ions or particles are of opposing electrical signs. That is, a suspension the particles of which carry negative charges will be flocculated only by a solution containing positive ions, and vice versa. Schulze (20) further states that the flocculating power of an ion increases very rapidly with its valence.

PROCTECTIVE COLLOIDS

It has been known for some time that the addition of small amounts of colloids belonging to the emulsion class greatly increase the stability of the suspension. Those that do this are given the special name of "protective colloids". They are much less sensitive to electrolytes than the suspensions, and their effect is explained by assuming that each particle of the suspension is coated with a thin layer of the emulsoid calloid, and then takes the electric charge of the latter. This action is important in explaining the plasticity of clays. The most important inorganic emulsiod is silicic acid. On the addition of Hcl to a sol of this acid it will set to a gel and the change

is not reversible. It was thought at first that this gel represented a definite hydrate, but the work of Ramsay, and Spring has shown that this is not a definite hydrate.

D INORGANIC COLLOIDAL MATTER

Schloesing is considered by many to be the first to demonstrate colloids as the cause of plasticity, and, since his time, many investigators have fallen in line with the colloidal theory of plasticity. Rohland (21) pointed out that colloids, as distinguished from the crystalloids, are substances that possess shrinkage and cohesion on drying, properties associated with the plasticity of clays.

Further, he summarizes plasticity as follows:

"Those substances that form colloidal solutions in water develop more or less plasticity. Clay and porcelain bodies contain colloids of both organic and inorganic nature, to a certain extent latent, the colloidal condition being only developed in water." The plasticity can be increased both by organic and inorganic colloids.

INORGANIC COLLOIDS.

Adsorption Theory.

Compounds of the silicic acid type have the important property of adsorption of other colloids and salts from solutions; hydrous gel bodies are shown to be present in clays by their degree of absorption.

Ashley's method of determining the colloidal content of clay is based upon their adsorptive phenomenon. In brief, the adsorptive theory evolved in the following manner: It was known early that a sol is coagulated when its static charge of elcricity is neutralized. This is generally done by electrolytes . When a negative siol , such as clay, has been brought into colloidal suspensions, the positive ion of the electrolyte added is the most influential in affecting precipitation, the acid ion taking little part. After a sol has been coagulated by a certain amount of an opposite ion, the question naturally presents itself as to what becomes of the excess of the coagulating ion or of other ions of the same sign that may subsequently be brought into the liquid. Some held that the exdess ions are collected on the surface of the gels, "absorbed", as is considered in the case with gases held by charcoal. Others believed that the excess ions are distributed between the outside liquid and the gel as if the gel were the second of the two immiscible liquids; that is that the ions were held in solid solution in the gel.

Hirsch (22) in his account of "The behavior of clay in salt solutions", saw the possibility of absorption He tried to classify clays according to their plasticity with the help of this process(absorption of brium chloride). His experiments with barium chloride were not successful. Ashley then tried the same process with malachite green. Further in this report the writer will outline the present

modification of Ashley's malchite green test under Chapter II. Ashley was able with his results of the malachite green test to establish a series of clays showing their relative plasticity from the amount of malchite green absorbed by them. In other words, he established the fact that colloids, organic and inorganic, are present in clays, more in some than in others, and that these colloids absorb the malchite green; therefore, the clay of greater colloidal content absorps more dye than a clay of less colloidal content, so that a clay high in colloid content is highly plastic and will absorp a greater quantity of malachite green, and vice versa.

COLLODIAL SILICA

It is well known that silicic acid when evaporated to form a jelly becomes viscous enough to effect plasticity. H. B. Davis experimenting with an excessive plastic clay of Western Canada attributes the plasticity to colloidal silica and organic colloids.

Van Bemmelen found that a silica gel of the formula $SiO_2.4H_2O$ retains aluminum chloride very teaciously.

IRON AND ALLUMINUM HYDROXIDE COLLOIDS.

Many investigators believe that colloidal ferric and aluminum hydroxide as the cause of plasticity. In 1868 Warrington (23) found that ferric and aluminum hydroxide capable of absorping potash and ammonia.

N. B. Davis (24) states in his summary of the literature on plasticity of clay the following:

1 - In the decomposition of rock minerals to form clay, the crystalline minerals under the influence of water and other agencies, tend to form colloidal modifications, soluble salts, and more crystalline complexes.

2 - The common colloidal sols formed are those of silicic acid, alumina, and iron hydrate.

3 - When formed these sols tend to coagulate one another and form gels. These sols and gels remain in part, coating the mineral grains.

E - ORGANIC COLLOIDS IN GENERAL

In 1904 Ries (25) writes "it may seem doubtfull whether interlocking of grains alone is sufficient to account for the tenacity of the clay, and whether or not organic substances, included under the term of colloids and which are no doubt present in many clays, do not exert some cementing influence.

Davis (26) likewise attributes plasticity as influenced by organic matter. He found by mixing Delaware washed Kaolin, water, and peat in a ball mill the plasticity of the Kaolin was somewhat increased.

Acheson (27) found that an addition of tannin to a clay increased its plasticity.

ORGANIC COMPOUNDS OF IRON AND ALUMINUM.

John Stewart (28) says, "Taking all facts into consideration the plasticity of clay is due to the presence of organic aluminum compounds. This explains why it is that impure and not pure clays that are plastic; why ignition destroys plasticity and why levigation fails to restore plasticity of the ignited clays and why clays are subjected to weathering before use in the ceramic arts." Stewart then sums up his arguments with the statement "my explanation of the plasticity is correct and that organic compounds of alumina are the only important ones concerned in this phenomenon, other compounds may contribute to the plasticity of very impure clays in a minor degree.

Sources of organic matter.

A resume' of the sources of organic matter of soils will now be outlined. We have only to take one step further, from soil to clay or shale, and we see that many of the compounds existing in a soil may be found in either clay or soil. The process of formation of clay permits us to reason so. We see every day the material carried by streams and rivers. The Mississippi River is a good example of a large river carrying to its mouth immense amounts of debris is which are tons of animal and

vegitable remains, to be deposited in the form of deltas from which shale will be formed in the ordinary process or rock formation. Streams like the one mentioned, and some by far larger, existed before man kind. Similar processes took place. Erosion by early seas caused similar deposition but on larger scale. Not only was there rock eroded and carried away but also existing siols formed by the process to be described. That plants and animals existed is former times we know from our coal deposits, our deposits of oil and gas, and the innumerable quantity of plant and animal fosils found in rocks.

(29) The essential difference between soil and mere mass of disintergrated rock is that the former contains some organic matter. The first step in the formation of bare rock into soil must be accomplished by the lowest form of plant life, which obtains the material necessary for their grouth and reproduction from the air, rain water and mineral matter dissolved in the rock. The death of these furnishes organic matter which can be utilized by higher forms, and the process goes on until there is an accumulation of organic matter sufficient, with the disintergrated rock material to be called an arable soil and furnishes a medium suitable for the grouth of higher plants.

When the process of soil formation has reached this stage the number of micro-organisms, which were at first confined to a few species, is greatly increased including bacteria and fungi of widely varying habits of grouth and varied products resulting from their grouth. There is, then, entering into the organic matter of a soil on which wild plants or crops are growing the remains of such parts of these plants as die and any products from the living plants. Still other compounds result from these through the growth of micro-organisms, and finally there are remains of the micro-organisms themselves.

It is usual to consider the organic matter of plants and animals as made up of protein, fat, and carbohydrates, but in addition to these elements there are, particularly in plants, a host of other compounds not included in these groups and which are a source of no small part of the soil organic matter. Amoung these are resins, hydrocarbons and derivatives, waxes, alkaloids, glucosides, tannins, phenols, and their defivatives, acids, aldhydes, etc.

F - HUMUS MATTER

The term "humus", as ordinarily used, has no especial scientific significance, being simply another name for dark colored vegitable matter or mold and later to this mold material as a constituent more or less

lls.

The term has not a more restricted meaning, es-

is used by agricultural chemists, being applied to

the dark-colored organic matter extracted from soils and dilute solutions of sodium or amonium hydrate and often called humus acids.

Mulder (30) divided these bodies into two groups, one group consisting of crenic and apocrenic acids, and the other of geic, humic, and ulmic and ulmin acids. Since Mulder's time various investigators have reached different conclusions, It is not the purpose of the writer to go into the history of the evolution of humus compounds. The reader is refered to books on agriculture chemistry. However, if humus prepared from a soil, or as the writer has done from a shale, in the clay laberatory of Kansas University, in the usual way by extracting the shale with dilute alkali and precipitating these bodies from the solutions so obtained by acid, their results, and thoroughly washing this precipitate, a body or mixture containing carbon, hydrogen, oxygen, and some ash ingredients. If this precipitate is again disolved in alkali and precipitated again there is obtained a mixture containing carbon, hydrogen, oxygen, and nitrogen in quite different proportion from the first precipitate. It is of interest to note in this connection that if this is repeated several times a point is reached where the humus precipitates becomes colloidal and passes through the filler.

The only conclusion reached from the survey of the literature is that humic acid and allied bodies are mixtures of unkown compounds, and that if there is a single compound making up the major portion of the so-called humic acid, it is as yet of unkown composition, constitution, and properties, and that these bodies whatever they may be may be defined as those dark colored amorphous compounds ~~ar~~ arising through the decay of organic matter. In this group, then, would be included those soluble in alkalies, ~~the so~~ called ulmic and humic acids, and those insoluble in alkalies known as ulmin and humin.

Summing up this survey of the literature, it might be stated that the humus bodies are a group of compound of unkown composition and constitution, some of which seem resemble the natural animal pigment known as malanins, themselves bodies of indefinite composition and unknown constitution, apparently of protein nature. There is some evidence that animo compounds are present in some of the soils. The presence of waxes, resins, and other difficult decomposible plant residue is indicated and finally there is the isolation of a single nitrogenous compound picolene carboxylic acid, which doubtless constitutes but a very small portion of the organic matter.

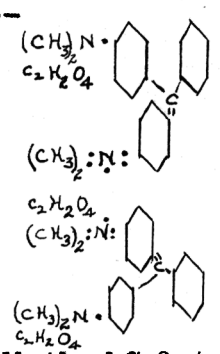
The amount of organic matter in ordinary soil is appreciably large, the average organic content of soils is 2.06 per cent. If the soil is taken as eight inches

deep, there would be an average of twenty-eighttons of organic matter in the soil per acre, and fifty tons in the soil and subsoil to the depth of two feet. If such large amounts exist in soil it can readily be seen that a large fraction, at least, of the organic material is ~~the~~ deposited in the process of formationof shales and clays.

CHAPTER II.

MALACHITE GREEN TEST FOR GAUGING THE COLLOIDAL MATTER OF CLAY

As was stated before, by gauging the colloidal content of the clay, or a series of clays, and comparing it to the amount of colloids in a standard clay relative plasticity may be established, Malachite green (oxalate) is a dye of the composition $(C_{23}H_{24}N_2)_2(C_2H_2O_4)_3$ (31) of which the molecular weight is 890.6, or per one color base ion, 445.3 . The structual formulaof malachite green is written thus



Method of testing.

In a 200 cc. glass cylinder provided with a glass stopper 50cc of water was put. to this was added one gram of clay, ground to pass 60 mesh screen. 50cc malachite green solution (6 grams malachite green oxalate per liter) was then added. The cyliders were then placed in a mechanical shaking machine, making 30 revolutions per minute. After shaking for two hours the cylinders were removed and allowed to settle over night. (The machine for this purpose was constructed by Mr. Paul Teetor). On the following morning one cc of the super natant liquid was taken out with a pipette, the tip of which was inserted

View of shaking machine and Schreiner colorimeter for gauging colloidal content of clays.

A - Schreiner's Colorimeter.

B - Shaking machine with glass cylinders.

to the 60 cc mark on the cylinder, and run into one of the cylinders of a Schreiners Colorimeter (a view of the colorimeter and shaking machine is shown on the next page). into the other cylinder of the calorimeter.5 cc of the standard dying solution (6 grams per liter) was placed, and to both cylinders water was added to dilute the malachite green to 50 cc.

With the use of a Shreiners Calorimeter direct reading can be obtained without further dilution. By moving one or the other of the cylinders up or down, a point is reached whereby the colors in both cylinders, as seen in the miror of the colorimeter, are of the same intensity. Then by reading the graduations on the cylinders, between the bottom of the outer cylinder and the bottom of the inner cylinder, we obtained a relative intensity of color of both solutions.

Calculation of results.

The standard malachite green solutions contains 6 grams of malachite green oxalate per liter. Therefore 50 cc of the solution added to one gram of clay contains 0.3 grams malachite green oxalate.

Under color comparison in Table I.

0.5 c.c. (Containing 0.003 grams of malachite green) of standard solution was added to one of the cylinders of the calorimeter, this was diluted to 50 cc. 1 cc. of malachite green, taken from the cylinder containing the treated clay sample, was placed in the other cylinder of the colorimeter, and this likewise diluted

TABLE I.

Colorimeter Readings.

No. Clay	Wt. Clay grams	c.c. dye solution added	COLOR COMPARISON Stand. c.c. taken	Stand. diluted to	Test c.c. taken	Test diluted to	Colorimeter Readings Stand.	Colorimeter Readings Test.
199	1.00	50.00	0.5	50.0	1.0	50.	12.	30.0
198	1.00	50.00	0.5	50.0	1.0	50.	11.0	26.3
173	1.00	50.00	0.5	50.0	1.0	50.	15.5	32.0
Tenn.ball	1.00	50.00	0.5	50.0	1.0	50.	13.0	26.0
129	1.00	50.00	0.5	50.0	1.0	50.	13.0	25.0
3	1.00	50.00	0.5	50.0	1.0	50.	16.3	27.6
187	1.00	50.00	0.5	50.0	1.0	50.	16.0	27.0
197	1.00	50.00	0.5	50.0	1.0	50.	15.0	25.0
5	1.00	50.00	0.5	50.0	1.0	50.	18.0	30.0
195	1.00	50.00	0.5	50.0	1.0	50.	12.5	20.0
137	1.00	50.00	0.5	50.0	1.0	50.	15.6	24.3
178	1.00	50.00	0.5	50.0	1.0	50.	20.5	3110
193	1.00	50.00	0.5	50.0	1.0	50.	20.5	31.0
194	1.00	50.00	0.5	50.0	1.0	50.	16.0	23.5
11	1.00	50.00	0.5	50.0	1.0	50.	16.0	23.5
177	1.00	50.00	0.5	50.0	1.0	50.	2.15	31.0
190	1.00	50.00	0.5	50.0	1.0	50.	19.5	28.0
191	1.00	50.00	0.5	50.0	1.0	50.	16.0	23.0
2	1.00	50.00	0.5	50.0	1.0	50.	14.6	20.6
132	1.00	50.00	0.5	50.0	1.0	50.	18.7	25.0
13	1.00	50.00	0.5	50.0	1.0	50.	14.5	19.5
196	1.00	50.00	0.5	50.0	1.0	50.	17.0	23.0
10	1.00	50.00	0.5	50.0	1.0	50.	2120	26.0
131	1.00	50.00	0.5	50.0	1.0	50.	20.0	25.0
9	1.00	50.00	0.5	50.0	1.0	50.	20.5	25.5
1	1.00	50.00	0.5	50.0	1.0	50.	22.5	26.5
184	1.00	50.00	0.5	50.0	1.0	50.	25.0	29.0

TABLE II

No. of Clay	Weight taken grams	c.c. of Dye Solution Added	Color Comparison				grams dye remaining in Solution		grams dye absorbed		Relative Plasticity
			Standard		Test						
			c.c. taken	diluted to	c.c. taken	Diluted to	Per. C.C.	Total	Total	Per. 1 gram clay	
199	1.0	50.0	0.5	50.0	1.0	50.0	.001200	.1200	.1800	.1800	120.00
198	1.0	50.0	0.5	50.0	1.0	50.0	.001253	.1253	.1747	.1747	116.40
173	1.0	50.0	0.5	50.0	1.0	50.0	.001452	.1452	.1548	.1548	103.20
Tenn. Ball	1.0	50.0	0.5	50.0	1.0	50.0	.001500	.1500	.1500	.1500	100.00
129	1.0	50.0	0.5	50.0	1.0	50.0	.001556	.1556	.1444	.1444	96.30
3	1.0	50.0	0.5	50.0	1.0	50.0	.001750	.1775	.1225	.1225	81.66
187	1.0	50.0	0.5	50.0	1.0	50.0	.001777	.1777	.1223	.1223	81.53
197	1.0	50.0	0.5	50.0	1.0	50.0	.001800	.1800	.1200	.1200	80.00
5	1.0	50.0	0.5	50.0	1.0	50.0	.001800	.1800	.1200	.1200	80.00
196	1.0	50.0	0.5	50.0	1.0	50.0	.001875	.1875	.1125	.1125	75.00
137	1.0	50.0	0.5	50.0	1.0	50.0	.001925	.1925	.1075	.1075	71.70
178	1.0	50.0	0.5	50.0	1.0	50.0	.001981	.1981	.1019	.1019	68.00
193	1.0	50.0	0.5	50.0	1.0	50.0	.001984	.1984	.1016	.1016	68.00
194	1.0	50.0	0.5	50.0	1.0	50.0	.003040	.2040	.0960	.0960	64.00

11	1.0	50.0	0.5	50.0	1.0	50.0
177	1.0	50.0	0.5	50.0	1.0	50.0
190	1.0	50.0	0.5	50.0	1.0	50.0
191	1.0	50.0	055	50.0	1.01	.50.0
2	1.0	50.0	0.5	50.0	1.0	50.0
132	1.0	50.0	0.5	50.0	1.0	50.0
13	1.0	50.0	0.5	50.0	1.0	50.0
196	1.0	50.0	0.5	50.0	1.0	50.0
10	1.0	50.0	0.5	50.0	1.0	50.0
131	1.0	50.0	0.5	50.0	1.0	50.0
9	1.0	50.0	0.5	50.0	1.0	50.0
1	1.0	50.0	0.5	50.0	1.0	50.0
184	1.0	50.0	0.5	50.0	1.0	50.0

.003042	.3042	.0958	.0958	63.86
.003080	.3080	.0920	.0920	61.30
.003088	.3088	.0912	.0912	60.80
.003090	.3090	.0910	.0910	60.66
.003116	.3116	.0884	.0884	58.90
.003166	.3166	.0834	.0834	55.60
.003230	.3230	.0770	.0770	51.30
.003270	.3270	.0730	.0730	48.70
.003345	.3345	.0655	.0655	43.70
.003400	.3400	.0600	.0600	40.00
.003411	.3411	.0589	.0589	39.30
.003490	.3490	.0510	.0510	34.00
.003585	.3585	.0415	.0415	27.66

to 50 c.c. Having found the colors of both cylinders of equal intensity, the readings were found to be for Tennessee Ball Clay #3 ;

Reading on cylinders:

Standard cylinder -- 13

Test cylinder -- 26

The number of grams of dye in 1 c.c. of test solution is then $0.003 \times 13 = X \times 26$

$$X = \frac{0.003 \times 13}{26} = 0.0015 \text{ grams.}$$

1 c.c. of test solution contains 0.0015 grams of dye
100.c.c." " " " 0.15 " " " "

0.30 grams of dye in 50 c.c. added to 1 gram of clay
0.15 " " " remained in the solution

0.15 grams of dye absorped by the colloids in 1 gram of clay

In this manner, the entire series of clay were calculated from the readings of the colorimeter, Table No. 1 shows the colorimeter readings, table No 2 shows the calculated data and the plasticity of the Dakota clays.

The malachite green tests does not give the colloidal matter directly, but by comparison with the absorption found under similar conditions with a very plastic clay as a standard (for which purpose Tennessee Ball clay #3 was used) the relative plasticity may be guaged.. For example Tennessee Bal clay absorped 0.15 grams of dye and is considered 100 in plasticity, then clay 199, having absorped 0.18 grams of dye, has therefore a relative plasticity equal

to $\frac{0.18}{0.15}$ x 100 or 120. In this way table No. 2 was completed, by comparing the amount of dye absorped by each clay against Tennessee Ball clay as the standard.

The absorption of malachite green is in all probability an exchange of bases. The dye is a salt of a complex ammonia base which forms in soluable compound with the colloidal acid radicals while its oxidate radical forms in soluable oxalates with the bases which tends to keep the clay coagulated. Therefore its reaction with the colloidal matter is very complete. It fails, indeed (is decolorized), with alkaline and limy clays. As both the sulphide and chloride of this dye is soluable in water, no serious interference can be ascribed to such soluable salts as occur in clays. No other dye is so free from objections and so well suited for colloidal measurment. (32)

The clays used in these experiments are of the Dakota formation of Kansas, and they were taken from the following counties.

Ottawa County
187
195
193
194
190
191
196
194

Cloud County
199
198
197

TABLE III

No. of clay	Degree of relative plasticity.	Arragement of clays by No. according to "feel test"
199	120.00	198
198	116.40	199
173	103.20	Tenn. Ball
Tennessee ball Clay.	100.00	197
129	96.30	195
3	81.60	178
187	81.53	196
197	80.00	173
5	80.00	5
195	75.00	132
137	71.70	129
178	68.00	191
193	68.00	3
194	64.00	194
11	63.86	10
177	61.30	137
190	60.80	177
191	60.66	11
2	58.90	131
132	55.60	187
13	51130	190
196	48.70	9
10	43.70	184
131	40.00	193
9	39.30	1
1	34.00	2
184	27.66	13

tear apart.

The Dakota clays were arranged in their ofder of plasticity by the"feel test" as accurately as possible and as a whole they check reasonably well with the malachite green test results. Several of the clays have almost the same plasticity. However, since the feel test involves the personal factor, several of the clays in the middle of the series are somewhat disturbed in relation to the order shown by the table under the malachite green test.

The most plastic clays according to the feel test are also the most plastic under the malachite green test, and the least under the feel test are also shown to be the least plastic under the malachite green test. Below is shown a table of comparison between the feel test and the malachite green test. There is one notable exception in the feel test in clay 196, this being very plastic in the feel test but of low absorption, in the malachite green test.

"Shrinkage test"

Method of testing .

To show the drying shrinkage of a clay, it is developed to working properties by mixing with water, then moulded into a small briquette. (6.76c.M. X 2.c.m. X 2 c.m.)

Shrinkage marks 6 c.m. apart were placed on the briquette as soon as it was removed from the mould. The briquette was allowed to dry and after drying the shrinkage was measured and calculated in percent of the dry length.

Experience seems to show that there is a relation between the shrinkage of a clay and its plasticity and it still remains to be shown whether the relation is a simple or complex function. From our knowledge of colloids we would expect a clay having a high colloidal content to have a high shrinkage, and as a general rule this is borne out in practice. We have a right to consider that colloids are present in clays for the following reasons;
Colloids when moistened with water expand or swell and on drying shrink again. Upon remoistening with water they do not develope their original amount of swelling. This experience is quite common in the ceramic industry, especially in the porcelain factory. Colloids show adsorption and clays do likewise.

The colloids of a clay may be either of the "gel" or "set-gel" form. They are to a certain extent reversible, the "gel" can be changed to the "set-gel"form by heating, while the "set-gel" can be changed to the "gel" form by grinding with water.
Returning to our former statement, that colloids show shrinkage on drying as do clays, it is, therefore, very evident that there is a relation between shrinkage and colloidal content.

Inorder to correlate the relation between the malachite green test, used to show the relative plasticity of the Dakota clays, and their shrinkage, those results have been plotted, the ordinate shows the malachite green results while the abcissa shows the linear drying shrinkage. It will be noted that with the exception of clays 186, 191, and 184 the clays follow a regular curve fromthe lean clays near the origin upto the very plastic clays. The curve seems to indicate that the linear drying shrinkage of a clay does not increase as rapidly in proportion to the relative plasticity as determined by the maiachite green test.

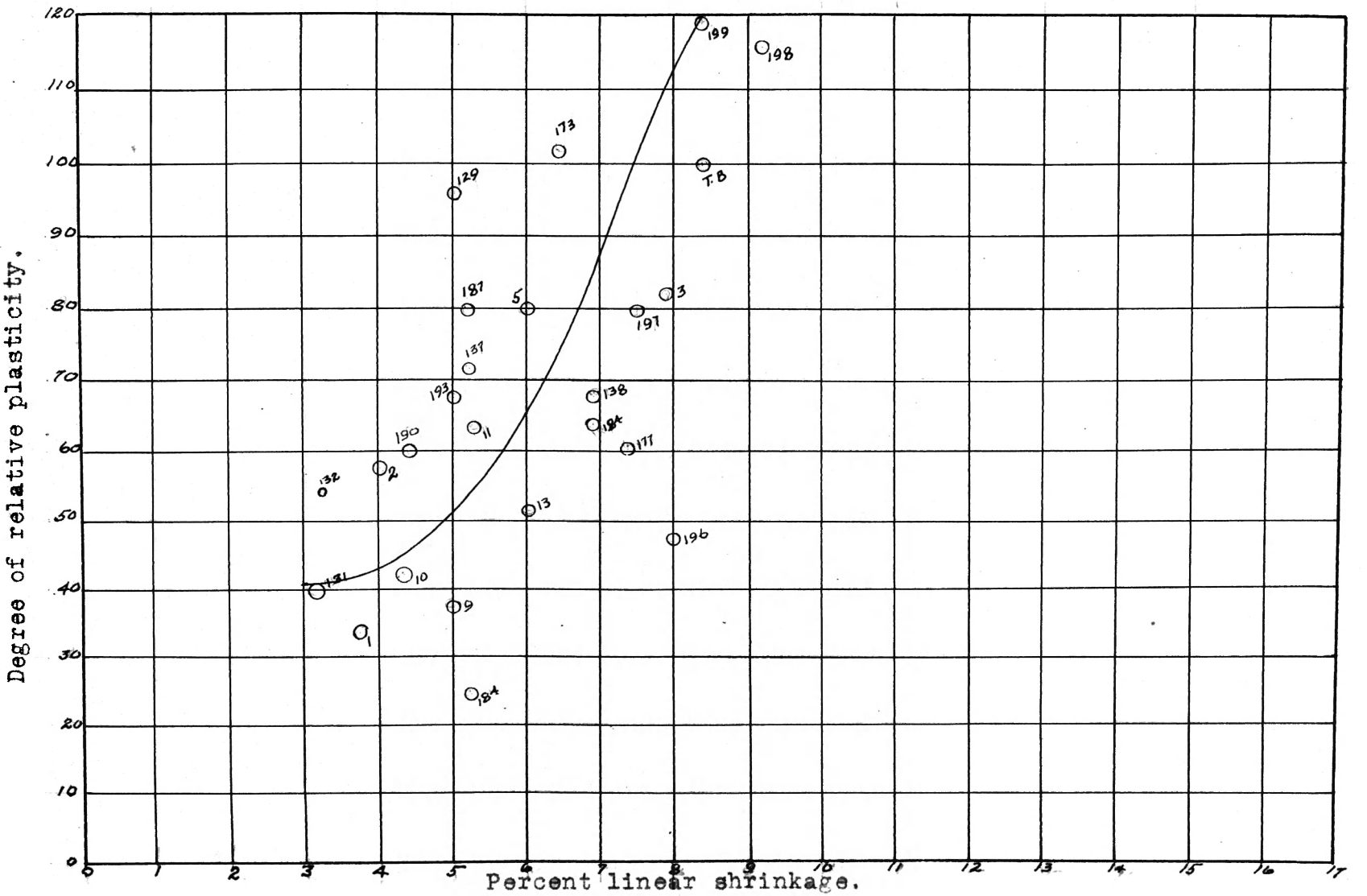
There are various physical explanations for the above statement. However, the writer will endeavor to explain this difference by the physico-chemical changes involved in carrying out both the shrinkage and malachite green tests. The malachite green test depends upon the property of colloids to absorb a dye, malachite green in this case. It makes no difference in this test whether the colloids in the clay are organic or inorganic.

The shrinkage test depends upon the property of a clay to absorb water and upon drying to give off the absorped water. In this case, too, the colloidal matter is in the clay is the absorbent of the added water. However, the essential difference lies in this fact namely, that the kind of colloids in the clay is the essectial factor. Thus, a clay with only organic colloids will show the same plasticity, ~~as determined~~

TABLE IV

No. of clay	Relative Plasticity	Percent linear drying shrinkage.
199	120.00	8.50
198	116.40	9.08
173	103.20	6.66
Tenn. Ball	100.00	8.50
129	96.30	5.00
3	81.66	7.91
187	81.53	5.26
197	80.00	7.33
5	80.00	6.00
195	75.00	6.00
137	71.70	5.26
178	68.00	6.95
193	68.00	4.98
194	64.00	6.66
11	63.86	5.44
177	61.30	7.55
190	60.80	4.31
191	60.66	10.94
2	58.90	4.16
132	55.60	3.36
13	51.30	5.82
196	48.70	7.52
10	43.70	4.34
131	40.00	3.12
9	39.30	4.92
1	34.00	3.80
184	27.66	5.26

Curve showing relation between plasticity and drying shrinkage.



as determined by the malachite green test, as will a clay with an equal amount of only inorganic colloids. The shrinkage determinations of the two clays will, however, vary to a certain extent. The reason for such variation is easily explained when we understand the physical properties of the organic and inorganic colloids. In the case of the clay that contains colloids of organic nature the water absorbed in making the shrinkage test is readily given off when the clay drys, there is no chemical action between the colloids and the water. It is merely a physical action, a swelling of the organic colloids and returning to its original state when the water is evaporated on drying. In a clay that contains chiefly inorganic colloids the reaction between the water and the inorganic colloids may act in such a way that the colloids may change from an ordinary "gel"condition to that of the "set-gel" condition. In so doing the total quantity of water absorped will not be given off on drying, thus producing a variation from the result shown by the malachite green test. This is borne out by the results of clays 197 and 5. The two clays come from two different counties, the former from Cloud County and the latter from Ellis county. Clay 197 shows a relative plasticity of 80.00, and clay 5 shows also a relative plasticity of 80.00. Clay 197 has a drying linear shrinkage of 7.33 percent while clay 5 has a drying linear shrinkage of only 6.00 percent. To make this point clearer another example can be cited. Clay 5 and 195 both show equal shrinkage

results, (6.00%) yet they differ in their plasticity; clay 5 has a relative plasticity of 80.00 and clay #195 has a relative plasticity of 75.00. The variation in plasticity means that they vary in their amounts of colloidal matter, but clay # 5, which has the greater plasticity, may have, however, more inorganic colloidal matter so that its shrinkage is reduced in amount equal that of clay # 195.

SUMMARY

The malachite green test yields a good comparative measure of the plasticity of clays. It is also provides a rapid and easy method for determining the amount of colloidal matter in a given clay when compared to a standard clay, for example Tennesses Ball #3.

The series of Dakota clays tabulated in this paper shows, with two exceptions a wide degree of variation in plasticity. This same variation is also established by both the "feel test" and the shrinkage test.

In conclusion, it may be stated that this series of clays taken from the same formation (Dakota), and many from the same locality, and even from the same bed shows a marked degree of variation in plasticity.

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